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THE INVESTIGATION OF SPIN-CROSSOVER IN TETRANUCLEAR IRON (II) COMPLEXES BY MAGNETIC MEASUREMENTS

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Abstract. The synthesis of iron (II) tetrahedral complexes was carried out under carefully controlled conditions, using precisely selected chemical reagents and specific reaction parameters. After completing the synthesis, the structural integrity of the complexes was confirmed through elemental analysis, which verified the presence of the main elements in the crystals, ensuring the accuracy of the synthesis and confirming the desired composition of the obtained compounds.

Following the synthesis, a series of magnetic measurements was performed on the monocrystalline samples to study their magnetic properties in detail. These measurements were particularly focused on investigating the spin crossover behavior, which is an important phenomenon that occurs in iron (II) complexes. This transition between low-spin and high-spin states under varying external conditions, such as temperature, plays

a key role in defining the magnetic properties of the compounds. The development of a detailed methodology for optimizing the synthesis conditions was a crucial part of the research. It allowed for the production of complexes with high purity and yield, ensuring reliable and reproducible results in subsequent measurements and studies.

Moreover, the impact of temperature changes on the spin crossover process was thoroughly investigated. The findings demonstrated that temperature significantly influences the spin states of the complexes, which is critical for practical applications. These results could have implications for the design of new materials with tunable magnetic properties, particularly in fields such as molecular electronics and spintronic devices.

Keywords: iron (II) complexes, magnetic measurements, spin -crossover.

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МАГНИТТІК ӨЛШЕУЛЕР ӘДІСІМЕН ТЕМІРДІҢ (II) ТӨРТЯДРОЛЫ КЕШЕНДЕРІНДЕ СПИН-КРОССОВЕРДІ ЗЕРТТЕУ

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Аннотация. Мақалада магниттік өлшеулер әдісі арқылы зерттелген темір (II) негізіндегі төртядролы кешендердің монокристалдарын алу нәтижелері ұсынылды. Кешендердің құрамындағы негізгі элементтерді анықтау үшін элементтік талдау жүргізіліп, олардың синтез сапасы расталды. Синтез процесі үшін арнайы әдістеме әзірленіп, темірдің (II) төртядролы кешендерін алу барысында қолданылатын оптимальды шарттар анықталды, бұл кешендердің кристалл сапасын жақсартуға және олардың физикалық-химиялық қасиеттерін бақылауға мүмкіндік берді.

Зерттеу барысында ерекше назар кешендердің температуралық өзгерістерге

қатысты қасиеттеріне аударылды, атап айтқанда, спин-кроссоверлік ауысулардың температураға тәуелділігі зерттелді. Температураның артуы немесе кемуі кешендердің спин-кроссоверіне елеулі әсер ететіні анықталды, бұл олардың магниттік қасиеттеріне әсер етеді. Бұл құбылыстардың зерттелуі кешендердің құрылымдық және электрондық ерекшеліктерін тереңірек түсінуге мүмкіндік берді, сондай-ақ олардың болашақта магниттік материалдар мен спинтроника салаларында практикалық қолдану мүмкіндіктерін зерттеуге негіз болады.

Аталған нәтижелер темірдің (II) төртядролы кешендерінің құрылымдық, магниттік және термодинамикалық қасиеттерін кеңінен зерттеуге жол ашып, олардың функционалдық мүмкіндіктерін қолдану перспективаларын көрсетеді.

Түйін сөздер: темір (II) кешендері, магниттік өлшеулер, спин-кроссовер.

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ИССЛЕДОВАНИЕ СПИН-КРОССОВЕРА В ТЕТРАЯДЕРНЫХ КОМПЛЕКСАХ ЖЕЛЕЗА (II) МЕТОДОМ МАГНИТНЫХ ИЗМЕРЕНИЙ

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Аннотация. Представлены результаты синтеза тетраядерных комплексов железа (II), проведённого с использованием тщательно подобранных химических реагентов и специфических условий реакции, что обеспечило высокое качество получаемых продуктов. После завершения синтеза была проведена серия магнитных измерений на монокристаллах, что позволило детально исследовать их магнитные свойства. Особое внимание было уделено спин-кроссоверу — важному феномену, который характеризует переход между низкоспиновыми и высокоспиновыми состояниями в зависимости от внешних факторов, таких как

температура. Этот переход является ключевым аспектом в понимании магнитных характеристик исследуемых соединений.

Для подтверждения состава синтезированных комплексов был проведён элементный анализ, который подтвердил наличие всех основных элементов и правильность синтеза. Это дало возможность удостовериться в соответствии полученных соединений ожидаемым структурам и обеспечить высокую достоверность полученных результатов. Одной из значительных частей работы стала разработка методики синтеза, которая включала оптимизацию условий для получения тетраядерных комплексов железа (II). Благодаря этому была достигнута высокая степень чистоты и эффективность процесса, что обеспечило воспроизводимость результатов.

Дополнительно было исследовано влияние температуры на процесс спин-кроссовера, что позволило выявить значительное воздействие температурных изменений на спиновые состояния. Это имеет большое значение для разработки новых материалов с регулируемыми магнитными свойствами, что может найти применение в передовых технологиях, таких как спинтроника и молекулярная электроника.

Ключевые слова: комплексы железа (II), магнитные измерения, спин-кроссовер.

Introduction. Spin crossover (SCO) is a magnetic property of molecular and extended solids that can be observed for some compounds of d^4-d^7 transition metal ions. These ions can adopt electron configurations with different numbers of unpaired electrons; hence their compounds can undergo SCO between a low spin (LS) and a high spin (HS) state under external stimuli such as a change in temperature or pressure or photoexcitation. Cooperativity may lead to bistability in SCO materials, which is especially appealing for applications in information storage. The quest for materials useful for such applications explains the extensive research carried out on SCO complexes over the last half a century. These research efforts have been dominated by studies of Fe (II) complexes, which account for ~90% of known SCO compounds (Cambi, et al.,1931).

It was only in the early 1960s, about three decades after Cambi's discovery of the first spin state interconversion in iron (III) complexes, that the SCO phenomenon was reported to occur also in iron (II) compounds. The first SCO compounds of iron (II) described in the literature are $[Fe(phen)_2X_2]$ (phen = 1,10-phenanthroline; X = NCS, NCSe), frequently called the "classical" iron (II) SCO complexes. Extensive research activities began thereafter in this area, particularly favored by the discovery of the Mössbauer effect (recoilless nuclear resonance absorption) by Rudolf L. Mössbauer at nearly the same time. This nuclear resonance effect formed the basis for the development of a new spectroscopic technique, Mössbauer spectroscopy, for the detection of hyperfine interactions, which turned out to be extremely powerful for the characterization of iron-containing substances (Gütlich , et al., 2012; Gütlich, et al., 2013).

SCO occurs mainly for six-coordinate iron (II) compounds involving the change of electron configuration $t_{2g}^{6}e_{g}^{0}$ ($^{1}A_{1g}$, LS) ↔ $t_{2g}^{4}e_{g}^{2}$ ($^{5}T_{2g}$, HS). Many review articles describing the preparation, structure, chemical, and physical properties of SCO systems of iron (II) have appeared in the literature. Most iron (II) SCO systems possess an [FeN_6] coordination center (Halcrow, et al., 2013; Nihei, et al., 2008; Li, et al., 2011).

For many years, scientists have been intrigued by the magnetic characteristics of many substances and materials. It became evident at the start of the 20th century that these characteristics are the result of coordinated actions at the atomic and molecular levels. The origin of magnetism and the nature of the chemical bond become intrinsically intertwined with the advancement of quantum mechanics. It became clear that the item under study's magnetic properties depended on the fine structure's crystal chemistry peculiarities in the vicinity of atoms with unpaired electrons. This indicates that before X-ray diffraction analysis became popularity among researchers, the study of magnetic characteristics developed into a potent method for learning about the structure of inorganic substances. Scientists and chemists worked together to create magnetochemistry, a unique area of inorganic and coordination chemistry that has produced a wealth of information on the connection between an object's structure and magnetic characteristics (Weber , et al., 2010; Hilfiger et al., 2010).

Molecular magnetism is a new frontier in magnetochemical research that emerged from the utilization of magneto-structural correlations mainly for analytical reasons to the potential to create materials with specified magnetic characteristics. Significant progress has been made in this area during the last few decades. Molecular organic ferromagnets emerged, spin-crossover phenomenon was discovered, and investigations into spintronics and molecular electronics objects were conducted (Oshio, et al., 2000; Oshio, et al., 2003).

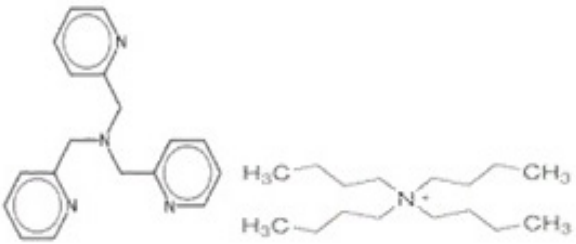
In the field of molecular bistability, spin-crossover (SCO) has been the subject of much investigation since it was first discovered in 1930 (Anderegg, et al.,1967). This phenomenon is a changeover between two electronic structures with different spin states. Ninety percent of known spin-crossover materials are iron (II) complexes. Complexes comprising d^4-d^7 transition metal ions now show differences between low-spin (LS) and high-spin (HS) electronic configurations (Tyeklar, et al.,1993). In these complexes, donor ligands containing nitrogen are commonly included in the coordination environment around the iron (II) ion, creating an intermediate ligand field that is favorable for spin-crossover processes. Variations in pressure, temperature, or photoexcitation can all cause spin transitions (Shatruk, et al., 2007).

Since the spin transition entails a change in the number of unpaired electrons—which is particularly noticeable in the case of iron (II) with its four unpaired electrons, where the low-spin (LS) state displays diamagnetism and the high-spin (HS) state displays paramagnetism - the main technique for describing spin-crossover (SCO) compounds is always to measure the magnetic susceptibility as a function of temperature, or χ (T).

In the liquid state, for example, the Evans NMR approach is frequently used; in the solid state, superconducting quantum interference sensors (SQUID, Superconducting

Quantum Interference Device) or the Faraday method are usually used. Palacio and associates offer a thorough synopsis of the techniques utilized in magnetochemistry (Hilfiger, et al., 2010).

The technique depends on determining the proportionate relationship between the sample's susceptibility and the fraction of the material in the high-spin state in order to generate the spin-transition curve. But it's important to understand that whereas the spin transfer is a property unique to individual molecules, magnetism applies to the entire bulk material. The presence of a spin transition cannot be established only by a change in magnetism (Berlinguette, et al.,2005). The complexes $\{[Fe(tpma)(\mu\text{-}CN)]_4\}X_4$ are the focus of the study, where X = ClO_4− (1a), BF_4− (1b); tpma = tris(2-pyridylmethyl)-amine. The $\{Fe(tpma)\}^{2+}$ building block was reacted with $(Bu_4N)CN$ to create these complexes (Figure 1).



A B

Figure 1.Ligands: A - Tris – (2-pyridylmethyl)amine (tpma); B - Tetrabutylammonium cyanide

The effective basis for inducing spin-crossover (SCO) in iron (II) complexes is provided by this combination of ligands. The spin-crossover transition in the studied complexes was the main focus of the investigation.

Materials and methods. The reactions were carried out using Schlenk's standard procedures in an inert nitrogen environment. Every reagent was purchased from Aldrich and used exactly as it was intended.

The synthesis of the complex $\{[Fe(tpma)(\mu\text{-}CN)]_4\}(ClO_4)_4$ (1a) was carried out as follows: Four milliliters of methanol (MeOH) were used to dissolve a mixture of $Fe(ClO_4)_2 \cdot 6H_2O$ (0.168 g, 0.46 mmol) and tpma (0.134 g, 0.46 mmol). The resulting transparent yellow solution was added to a solution of $(Bu_4N)CN$ (0.124 g, 0.46 mmol) in 4 ml MeOH gradually while stirring. The solution quickly took on a rich crimson hue and began to precipitate orange material. The mixture was kept undisturbed for 30 minutes after the reagent addition was finished, after stirring it for 20 minutes. After filtering and vacuum-drying the orange precipitate, 0.118 g of the compound—or a 55% yield—were obtained.

Elemental analysis: calculated for $Fe_4Cl_4O_{18}N_{20}C_{76}H_{76}$ (1a·2H2O), %: C- 47.48 (47.44); H - 3.98 (4.13); N - 14.57 (14.28).

$\{[Fe(tpma)(\mu\text{-}CN)]_4\}(BF_4)_4$ (1b): The synthesis of complex 1b adhered to the procedure outlined for 1a, utilizing $Fe(BF_4)_2 \cdot 6H_2O$ (0.206 g, 0.610 mmol), tpma (0.177

g, 0.610 mmol), and $(Bu_4N)CN$ (0.164 g, 0.610 mmol) as reagents. The resulting compound yield was 0.144 g (51%).

Elemental analysis produced the subsequent values for $Fe_4F_{16}O_5N_{20}C_{76}B_4H_{82}$ ($1b \cdot 5H_2O$), %: C - 47.39 (calculated 47.45); H - 4.29 (calculated 4.13); N - 14.54 (calculated 14.50).

Magnetic Measurements.

A Superconducting Quantum Interference Device (SQUID)-equipped Quantum Design magnetometer (MPMS-XL) was employed to measure the magnetic susceptibility of polycrystalline materials, focusing on a series of tetranuclear iron (II) complexes. The susceptibility was measured across a wide temperature range from 1.8 to 300 K, using a constant magnetic field of 0.1 T. This range allows the detection of temperature-dependent phenomena, such as spin crossover behavior, which are key to understanding the magnetic properties of these materials. Diamagnetic corrections were applied to the collected data by subtracting diamagnetic adjustments derived from standard tabular values, which is essential for ensuring the accuracy and clarity of the magnetic results (Boldog, et al., 2009).

Results and discussion. The study focused on the synthesis of tetranuclear iron (II) complexes, denoted as $\{[Fe(tpma)(\mu\text{-}CN)]_4\}X_4$, where "tpma" stands for tris(2-pyridylmethyl)amine, a tetradentate ligand that stabilizes the iron centers. These complexes were synthesized by adding the tpma ligand to a prepared cyanide fragment, (Bu4N)CN, resulting in the formation of stable tetranuclear structures. The use of a single blocking ligand, tpma, allowed for a controlled assembly of the iron centers, forming the desired polynuclear complexes in crystalline form. Two distinct complexes were studied in detail: $\{[Fe(tpma)(\mu\text{-}CN)]_4\}(ClO_4)_4$ (denoted as 1a) and $\{[Fe(tpma)(\mu\text{-}CN)]_4\}(BF_4)_4$ (denoted as 1b).

Magnetic Properties. The magnetic properties of these complexes were thoroughly investigated through detailed magnetic susceptibility measurements, which were performed to gain a comprehensive understanding of the magnetic behavior of the complexes across a range of temperatures. These measurements are crucial for identifying how the complexes respond to temperature variations, providing critical insight into phenomena such as spin crossover—a thermally induced transition between low-spin and high-spin states. This transition is particularly significant in iron (II) complexes, where the spin state can dramatically impact the electronic and magnetic properties of the material.

For this study, dry powder samples of two specific complexes, designated as 1a and 1b, were carefully prepared and subjected to these magnetic susceptibility measurements. The experimental data obtained are presented in Figure 2, illustrating the temperature-dependent behavior of two essential parameters: χT, which denotes the product of the molar magnetic susceptibility and the absolute temperature, and γBC, a parameter specifically related to the dynamics of the spin crossover process. These parameters are invaluable for interpreting the magnetic behavior of the complexes, providing direct evidence of the changes in spin states of the iron centers in response to temperature variations.

At low temperatures, the results reveal that the complexes predominantly exist in a low-spin state configuration, which is characterized by relatively low χT values. This indicates that the unpaired electrons in the iron centers are minimized, leading to weaker overall magnetic interactions. As the temperature increases, a noticeable spin crossover is observed, shifting the complexes towards high-spin states. This transition is marked by a gradual increase in χT values, reflecting the enhancement of magnetic interactions due to the higher number of unpaired electrons in the high-spin state. The observed behavior suggests a gradual and continuous spin crossover, which is a common feature in polynuclear iron (II) complexes, where the cooperative effects between iron centers play a significant role in determining the magnetic properties.

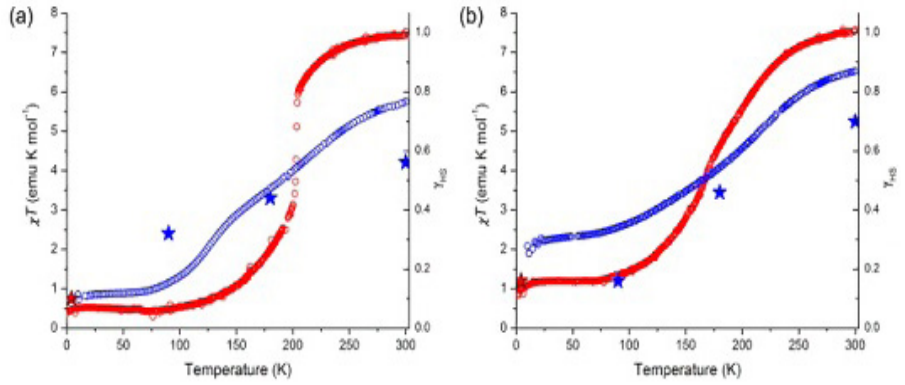


Figure 2. The temperature variation of χT and γBC for 1a and 1b complexes, recorded in a consistent magnetic field of 0.1 T.

The spin-crossover (SCO) for the aqueous samples 1a and 1b is more sudden and virtually complete in the case of the former compound, according to the study of the χT vs. T curves. Below 100 K, its χT value approaches a plateau of □0.5 emu K mol^{-1}. On the other hand, below 70 K, the aqueous sample 1b's χT value approaches a plateau of around 1.2 emu K mol^{-1}, suggesting that a considerable amount of the N_6-coordinated Fe (II) ions stay in the high-spin (HS) state even at low temperatures. The behavior of dry samples differs significantly, with the spin-crossover being considerably more gradual and incomplete at both high and low temperatures. For both 1a and 1b, the dry sample's residual low-temperature percentage of HS ions is greater than the watery sample's (Shatruk, et al., 2009; Hietsoi, et al., 2014; Kassenova, et al., 2014; Kassenova, et al., 2014).

Conclusions. The first known example of homoleptically-capped tetranuclear CN-bridged Fe (II) complexes that exhibit spin-crossover behavior is the {[(tpma)Fe(μ-CN)]$_4$}X_4 series, where X can be ClO_4^- (1a) or BF_4^- (1b). Interestingly, unlike typical dry samples of spin-crossover (SCO) Fe (II) compounds that usually display more abrupt transitions compared to their solvent-covered counterparts, these complexes demonstrate the opposite behavior, with more gradual transitions. This unexpected result may be attributed to the crystallinity of the samples, which could influence

the spin-crossover process. The study highlights the importance of investigating the magnetic properties of such materials in both their dry and mother liquor forms to fully understand their behavior. This distinction could provide insights into designing and optimizing materials for applications in fields where spin-crossover behavior is critical, such as molecular switches or memory storage devices.

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